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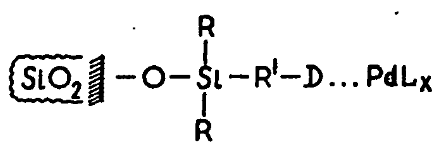
(71) Applicants
Institut Neftekhimicheskogo sinteza imeni A V Topchieva Akademii Nauk SSSR
Leninsky prospekt 29
Moscow
Union of Soviet Socialist Republics
Universitet Druzhby Narodov imeni Patrisa Lumumby
ulitsa Ordzhonikidze 3
Moscow
Union of Soviet Socialist Republics

(72) Inventors
Vladimir Mikhailovich Gryaznov
Viktor Sergeevich Smirnov
Valentin Mikhailovich Vdovin
Galina Konstantinovna Fedorova
Margarita Meerovna Ermilova
Lia Dmitrievna Gogua
Nina Andreevna Pritula

(74) Agents
Marks & Clerk
57–60 Lincoln's Inn Fields
London WC2A 3LS

(54) **Membrane catalyst for hydrogenation of organic compounds and method of preparing the same**

(57) A membrane catalyst for hydrogenation of organic compounds comprises a cermet substrate having deposited thereon, as a film, a product of interaction of a polyorganosiloxane polymer and a heterogenized palladium complex of the general formula:



wherein R is an alkyl group, an alkoxy group, or chlorine;

R' is $-C_6H_4-$, or $-(CH_2)_n-$ where $n = 1-10$;
D is $-PR_2'''$, where R''' is an alkyl or phenyl group;
or $-NR_2'''$, where R'' is an alkyl group;
or $-C_6H_4N$; and
L is $-C1$, $-Br$, or $-OCOH_3$.

Such a membrane catalyst is prepared by application onto a cermet substrate of a mixture of a polyorganosiloxane polymer and a heterogenized palladium complex of the above formula, and vulcanization thereof in the presence of a vulcanizing agent at a temperature of from 20 to 150°C until the formation of a film with a thickness of from 0.3 to 1.0mm occurs.

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SPECIFICATION

Membran catalyst for hydrog nati n of organic compounds and method of preparing the same

The present invention relates to a membrane catalyst for hydrogentation of organic compounds and to a method of preparing the same.

These catalysts are useful in the chemical and petrochemical industries owing to the possibility, obtained thereby, of carrying out two processes with detachment and addition of hydrogen without intermixing of the reaction products and at higher speed than on conventional catalysts.

There are known polymer-based compositions, employed for improvement of adsorption of hydrocarbons and separation of hydrogen isotopes.

U.S. Patent No. 2 722 504 teaches a composition consisting of a metal oxide (Al_2O_3, MoO_3, CuO, V_2O_5), an oxide or sulphide of a transition metal with an atomic weight of from 22 to 42, and silicone adapted for improvement of selective adsorption of hydrocarbons compared to oxide materials untreated with silicone.

U.S. Patent No. 3 981 976 teaches a composite catalyst for separation of hydrogen isotopes composed of a mixture of oxides of metals such as Al_2O_3, WO_3, MgO, and SiO_2, or of graphite with oxides of metals pertaining to Group VIII of the periodic system and a polymer possessing hydrophobic properties.

These known compositions, however, cannot serve as membrane catalysts selectively permeable to hydrogen.

At the present time, as hydrogen-permeable membrane catalysts use is made of palladium-based alloys manufactured as a foil, for example an alloy containing 85% by weight of Pd and 15% by weight of Pt (cf. Japanese Patent No. 11362), or as a tube (U.S. Patent No. 3 201 620). For the manufacture of such membranes a considerable consumprion of palladium per 1 cm^2 of the catalyst surface area is required. Thus, for the manufacture of a catalyst as taught in Japanese Patent No. 11362, it is required to use 0.24 g of palladium per 1 cm^2 of the catalyst surface; according to U.S. Patent No. 3 201 620, 0.20 g of Pd per 1 cm^2 of the catalyst surface area is required.

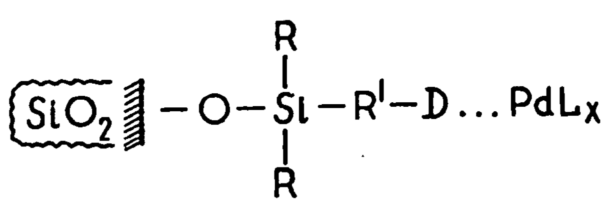
There is also known a method for producing a hydrogen-permeable membrane catalyst by rolling a foil with a thickness of from 0.05 to 0.1 mm composed of palladium or an alloy thereof (cf. Doklady Akademii Nauk SSSR, 211, No. 3, 624, 1973).

With a view to reducing the use of noble metals, there has been suggested a method for the manufacture of a membrane catalyst by sublimation of an alloy based on palladium onto a polymeric film selectively permeable for hydrogen; this film is applied onto a reinforcing substrate made of a cermet material and does not hinder penetration of the reagents (cf. USSR Inventor's Certificate No. 593351 of October 21, 1977; U.S. Patent No. 4 132 668).

This method makes it possible to produce a membrane catalyst in the form of a three-layered composition consisting of a cermet substrate based, for example, on copper, nickel or stainless steel, a polyorganosiloxane polymer film, and a thin layer of a catalytically active palladium-based component.

In this catalyst the catalytically active component is used insufficiently due to the non-uniform thickness of the layer of palladium over a large area of the catalyst. Furthermore, the size of this composite catalyst is limited, thus causing limitation of the unit capacity of a catalytic hydrogenation plant. The limited size of this catalyst is due to the small size of the vacuum chambers employed for sublimation of palladium. The composite membrane catalyst contains palladium or an alloy thereof in a low-disperse form, as a result of which the manufacture of a unit area of the catalyst surface involves the consumption of a rather great amount of palladium.

The present invention in one aspect provides a membrane catalyst for hydrogenation of organic compounds, comprising a metal-ceramic substrate having applied thereon, as a film, a product of interaction of a polyorganosiloxane polymer and a heterogenized palladium complex of the formula:



wherein R is an alkyl group, an alkoxy group, or chlorine;

R′ is $-C_6H_4-$, or $-(CH_2)_n-$ where $n = 1-10$;

D is $-PR''_2$, where R'' is an alkyl or phenyl gr up;
or $-NR'''_2$, where R''' is an alkyl group;
or $-C_6H_4N$; and
L is –Cl, –Br, or $-OCOCH_3$.

The membrane catalyst according to the invention has a high productivity per unit weight of palladium owing to the distribution of the active component throughout the volume of the membrane as well as owing to the possibility of ensuring substantiallv unlimited unit capacity of hydrogenation plants.

Furthermore, the catalyst according to the present invention possesses a combination of properties of both a hydrogenation catalyst and a hydrogen-permeable membrane, and also involves the use of a relatively low consumption of palladium in the manufacture thereof.

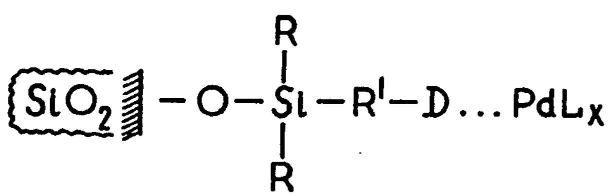
For improvement of the catalytic properties and hydrogen permeability, the membrane catalyst according to the present invention preferably comprises the following components taken in the following proportions, in per cent by weight:

cermet structure	50 to 89
polyorganosiloxane polymer	10 to 39
heterogenized palladium complex	1 to 4.

The membrane catalyst according to the present invention preferably contains in order to enhance its activity, as a film, product of interaction of a polyorganosiloxane polymer and a heterogenized palladium complex which is a complex compound of palladium attached to silica gel by means of chemically bonded (through a ≡Si–O–Si–C system of bonds) organosilicon ligands with nitrogen- or phosphorus-containing electron donor groups.

The thickness of the film in the catalyst is preferably from 0.3 to 1.0mm, in order to improve its hydrogen permeability.

The invention in another aspect provides a method of preparing a membrane catalyst for hydrogenation of organic compounds, comprising applying onto a metal-ceramic substrate a mixture of a polyorganosiloxane polymer and a heterogenized palladium complex of the formula:



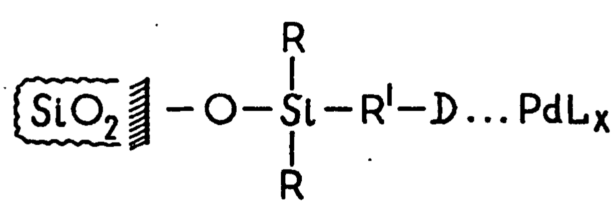
wherein R is an alkyl group, an alkoxy group, or chlorine;
R' is $-C_6H_4-$, or $-(CH_2)_n-$ where n = 1.10;
D is $-PR''_2$, where R'' is an alkyl or phenyl group;
or $-NR'''_2$, where R''' is an alkyl group;
or $-C_6H_4N$; and
L is –Cl, –Br, or $-OCOCH_3$
and effecting vulcanization thereof in the presence of a vulcanizing agent at a temperature of from 20 to 150°C until the formation of a film with a thickness of from 0.3 to 1.0mm occurs.

The method according to the present invention makes it possible to substantially simplify and shorten the duration of the catalyst manufacture due to the elimination of the stage of deposition, by spraying, of a catalytically active component based on palladium, the latter being introduced into the catalyst in the form of a heterogenized complex. The method according to the invention also permits the production of a catalyst of any size irrespective of the size of a high-vacuum spraying unit.

It is preferable to use, as the polyorganosiloxane polymer, polydimethylsiloxane or polymethylphenylsiloxane, containing 5 to 25 per cent by weight of phenyl groups.

The method according to the invention will now be described in more detail.

A catalytic component is preliminarily prepared, which is a heterogenized palladium complex of the general formula:



wherein R is an alkyl group, an alkoxy group, or chlorine;
R′ is $-C_6H_4-$, or $-(CH_2)_n-$ where n = 1–10;
D is $-PR''_2$, where R″ is an alkyl or phenyl group;
or $-NR'''_2$, where R‴ is an alkyl group;
or $-C_5H_4N$; and
L is $-Cl$, $-Br$, or $-OCOCH_3$.

For this purpose a modified inorganic oxide carrier, e.g. silica gel, is treated with a solution of a palladium salt, the inorganic carrier being modified with organosilicon compounds containing hydrolyzable groups attached to silicon and hydrocarbon radicals with functional groups capable of co-ordinating with compounds of metals of variable valency of the type: R_3 SiR′D, wherein R_3Si contains at least one hydrolyzable group, R′ is a hydrocarbon biradical, and D is a nitrogen- or phosphorus-containing group.

The resulting catalytically active component in the form of a heterogenized palladium complex is mixed with a polyorganosiloxane-α,ω-diol containing, as the vulcanizing agent, for example an aminosubstituted silane or alkyltriacetoxysilane and a filler such as zinc oxide, in a ratio of from 1:5 to 1:15 by weight. This mixture is applied in a thin layer (with a thickness of from 0.1 to 1.0mm) onto the surface of a cermet sheet material based, for example, on nickel, copper or stainless steel and subjected to vulcanization at a temperature from 20 to 150°C. The film formed as a result of the vulcanization of the mixture of an organosilicon polymer and a heterogenized palladium complex possesses characteristics of a hydrogenation catalyst and a hydrogen-permeable membrane. The thickness of the reinforcing substrate, a cermet material, is preferably varied within the range of from 0.1 to 1.0mm depending on the necessity of adjusting the gas-permeability of the whole composition. A thickness exceeding 1 mm may hinder hermetization of the membrane catalyst in a reactor, since upon increasing the material thickness metal-ceramic sheets become brittle. The use of a metal-ceramic sheet with a thickness of below 0.1mm may be limited by the high gas-permeability of the material. The hydrogen-permeability of the membrane catalyst is also adjusted by varying the thickness of the polyorganosiloxane film within the range of from 0.3 to 1.0 mm. Optimization of the properties of the polyorganosiloxane film is attained by varying the time, vulcanization temperature, type and quantity of the filler and vulcanizing agent. The catalyst productivity in reactions of hydrogenation of organic compounds can be adjusted by varying the ratio of the polyorganosiloxane polymer and heterogenized palladium complex within the range of from 5:1 to 15:1.

It is desirable to vary the proportions of the ingredients in the process of manufacture of the membrane catalyst in such a manner that the components be contained in the following amounts, in per cent by weight:

cermet substrate	50 to 89
polyorganosiloxane polymer	10 to 39
heterogenized palladium complex	1 to 4.

This membrane catalyst has a high catalytic activity and a high productivity per unit weight of palladium.

The resulting membrane catalyst comprises a bi-layered composition consisting of a layer of a porous cermet material employed as a reinforcing substrate and a thin polymeric film which is catalytically active and hydrogen-permeable; it also contains palladium in a highly active state, in contrast to membrane catalysts made of palladium alloys.

Consumption of palladium per 1 cm² of the surface area of the catalyst according to the present invention is 0.004g, or about 100 times less than in conventional membrane catalysts manufactured from palladium alloys.

The invention will be further described with reference to the following illustrative Examples.

EXAMPLE 1

To 2g of silica gel modified by dimethylethoxy (methyldiethylamino)silane in 60 ml of a benzene ethanol solution (1:1) there was added 0.6g of palladium chloride as a 40% aqueous solution. The reaction mixture was kept at room temperature for 24 hours. Then silica gel was filtered off, washed twice (50 ml each time) with a benzene-ethanol solution and twic (50 ml each time) with pur ethanol; thereafter silica gel was dried under a vacuum of 1.10^{-4} mm Hg during 6 hours at room temperature. A heterogenized complex with a palladium content of 2.2% by w ight was thus obtained.

0.18 g of the resulting catalyst with a particl size f less than 0.1 mm was mixed with 0.9 g of polydimethylsil xane-α,ω-diol containing zinc xid as a filler and methyltriacetoxysilane as a vulcanizing agent (in ratio of 3 parts by weight: 100 parts by weight of the polymer). This mixture was applied ont a sheet of porous c pper with dimensions of 119 × 22 × 0.1 mm. After vulcanization in air at room temperatur for two days the sample was placed under a vacuum of 10^{-3} mm Hg f r 6 hours t giv a polymeric film having a thickness of 0.3 mm.

The resulting membrane catalyst was mounted and sealed in a flow-type reactor adapted for carrying out hydrogenation reactions. To one side of the membrane catalyst was supplied hydrogen, while to the other side was supplied a mixture of cyclopentadiene vapour with argon at a rate of 10 ml/min. The partial pressure of the cyclopentadiene was 8.5 mm Hg, and that of hydrogen in the hydrogenation zone was 11.4 mm Hg. At a temperature of 161°C the conversion of cyclopentadiene was 89.9%, at the selectivity relative to cyclopentene of 0.95.

EXAMPLE 2

A membrane catalyst was produced by following the procedure as described in the foregoing Example 1, except that use was made of silica gel modified with dimethylethoxy(diphenylphosphinomethyl)silane. A heterogenized palladium complex with a content of palladium equal to 4.6 per cent by weight was obtained. A mixture of polydimethylsiloxane and heterogenized palladium complex in a ratio of 5:1 was applied as a 0.5 mm thick film onto a sheet of porous nickel of size 119 × 22 × 1 mm. The resulting catalyst had the following composition, in per cent by weight:

cermet material	—	76
polydimethylsiloxane polymer	—	20
palladium complex	—	4.

In a flow-type catalytic reactor, hydrogen was fed to one side of the membrane catalyst and a mixture of cyclopentadiene vapour with argon was fed to the other side of the membrane catalyst at a rate of 10 ml/min; the partial pressure of the cyclopentadiene in the reaction zone was 8.5 mm Hg, and that of hydrogen was 11.4 mm Hg at a temperature of 100°C. The achieved cyclopentadiene conversion was 86.6%, at a selectivity of 0.82 relative to cyclopentene.

EXAMPLE 3

On the basis of silica gel modified by triethoxy [β-(2-ethylpyridyl)] silane, by following the procedure described in Example 1, a heterogenized palladium complex was obtained containing 5.5% by weight of palladium.

Further, a membrane catalyst was prepared as described in Example 1, but the mixture of polydimethylsiloxane and palladium complex heterogenized on silica gel was applied as a 1 mm thick film onto a sheet of porous copper of size 119 × 22 × 0.5 mm. The resulting catalyst had the following composition, in per cent by weight:

cermet base	57
polydimethylsiloxane	39
heterogenized palladium complex	4.

This catalyst was employed in a reactor at a temperature of 88°C, the supply rate of cyclopentadiene vapour with argon being 10 ml/min, and the partial pressure of cyclopentadiene in the hydrogenation zone being 8.5 mm Hg and that of hydrogen being 11.4 mm Hg; a conversion of cyclopentadiene of 98.9% was attained, at a selectivity of 0.79 relative to cyclopentene.

EXAMPLE 4

A membrane catalyst was produced by following the procedure described in Example 2. A heterogenized palladium complex prepared on the basis of silica gel, modified by dimethylethoxy-(diphenylphosphinomethyl)silane, with a particle size of 0.1 mm, containing 2.8% by weight of palladium, was mixed with a polymethylphenysiloxane polymer (containing 5% of phenyl substituents at the silicon) in a ratio of 1:10 and applied onto a sheet of porous copper of size 119 × 22 × 0.5 mm. Vulcanization was conducted at a temperature of 25°C for 3 hours and then at a temperature of 150°C for one hour to obtain a film with a thickness of 0.3 mm. The resulting catalyst had th following composition, in per cent by weight:

cermet substrate	89
polydimethylphenylsiloxane	10
heterogenized palladium complex	1.

There was obtained on this catalyst in a reactor at a temperature of 100°C, the rate of supply of a mixture of cyclopentadiene vapour and argon being 10 ml/min, and th partial pressure in the zone of cyclopentadiene (CPD) hydrogenization being 8.5 mm Hg and that of hydrogen being 11.4 mm Hg, a conversion of CPD of 86.6%, at a selectivity of 0.82 relative to cycl pentene.

EXAMPLE 5

A membrane catalyst was produced as described in Example 1, the modification of silica gel being carried out with the use of dimethylethoxy (γ-diphenylphosphinopropyl)silane. A heterogenized palladium complex with a particle size of 0.1 mm containing 3.0% by weight of palladium was mixed with polydimethylsiloxane polymer in a ratio of 1:15 and applied onto a sheet of porous copper of size 119 × 22 × 0.5 mm. Vulcanization was conducted at a temperature of 25°C for 8 hours and then at 70°C for two hours to obtain a film with a thickness of 0.4 mm.

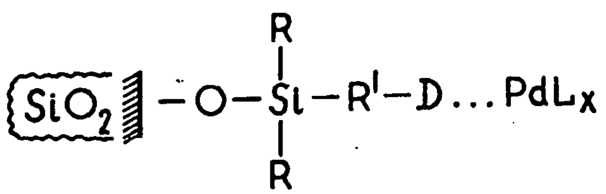
The thus-produced catalyst had the following composition, in per cent by weight:

cermet substrate	80
polydimethylsiloxane polymer	16
heterogenized palladium complex	4.

There was obtained on this catalyst in a reactor at a temperature of 20°C, the rate of supply of a mixture of cyclopentadiene vapour with argon being 10 ml/min, and the partial pressure of cyclopentadiene in the hydrogenation zone being 8.5 mm Hg and that of hydrogen being 11.4 mm, a conversion of cyclopentadiene of 97.7%, at a selectivity of 0.75 relative to cyclopentene.

CLAIMS

1. A membrane catalyst for hydrogenation of organic compounds, comprising a metal-ceramic substrate having applied thereon, as a film, a product of interaction of a polyorganosiloxane polymer and a heterogenized palladium complex of the formula:



wherein R is an alkyl group, an alkoxy group, or chlorine;

R' is $-C_6H_4-$, or $-(CH_2)_n-$ where n = 1–10;

D is $-PR''_2$, where R'' is an alkyl or phenyl group;

or $-NR'''_2$, where R''' is an alkyl group;

or $-C_5H_4N$; and

L is -Cl, -Br, or $-OCOCH_3$.

2. A membrane catalyst as claimed in Claim 1, comprising the following components in the following proportions, in per cent by weight:

cermet substrate	50 to 89
polyorganosiloxane polymer	10 to 39
heterogenized palladium complex	1 to 4.

3. A membrane catalyst as claimed in Claim 1 or 2, containing, as a film, a product of interaction of a polyorganosiloxane polymer and palladium complex heterogenized through a pyridinium ligand.

4. A membrane catalyst as claimed in Claim 1 or 2, containing, as a film, a product of interaction of a polyorganosiloxane polymer and palladium complex heterogenized through a tertiary amine ligand.

5. A membrane catalyst as claimed in Claim 1 or 2, containing, as a film, a product of interaction of a polyorganosiloxane polymer and a palladium complex heterogenized through a tertiary phosphine ligand.

6. A membrane catalyst as claimed in any of Claims 1 to 5, containing, as a film, a pr duct of interaction of a heterogenized complex of palladium and polydimethylsiloxane.

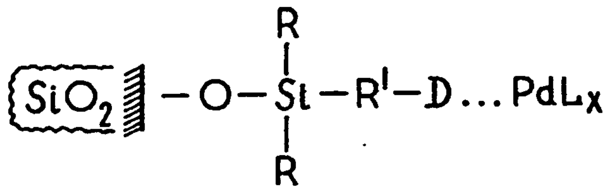
7. A membrane catalyst as claimed in any of Claims 1 to 5, containing, as a film, a product of interaction of a heterogenized complex f palladium and polymethylphenylsiloxane.

8. A membrane catalyst as claimed in any of Claims 1 t 7, wh rein the film thickness is equal to 0.3–1.0mm.

9. A membran catalyst according to Claim 1, substantially as her in described in any of the foregoing Examples.

10. A method of preparing a membrane catalyst for hydrogenation of organic compounds,

comprising applying onto a metal-ceramic substrate a mixture of a polyorganosiloxane polymer and a heterogenized palladium complex or the formuala:



wherein R is an alkyl group, an alkoxy group, or chlorine;

R' is $-C_6H_4-$, or $-(CH_2)_n-$ where n = 1–10;

D is $-PR''_2$, where R'' is an alkyl or phenyl group;

or $-NR'''_2$, where R''' is an alkyl group;

or $-C_5H_4N$; and

L is $-Cl$, $-Br$, or $-OCOCH_3$

and effecting vulcanization thereof in the presence of a vulcanizing agent at a temperature of from 20 to 150°C until the formation of a film with a thickness of from 0.3 to 1.0mm occurs.

11. A method as claimed in Claim 10, wherein the polyorganosiloxane polymer is polydimethylsiloxane.

12. A method as claimed in Claim 10, wherein the polyorganosiloxane polymer is polymethylphenylsiloxane.

13. A method according to Claim 1 of preparing a membrane catalyst, substantially as herein described in any of the foregoing Examples.

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